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Introduction to Hartree-Fock and CI Methods

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This lecture presents a short introduction to the most elementary concepts of wave function based quantum chemistry. In the first part, the molecular Hamiltonian is specified and the Born-Oppenheimer approximation is made. Thereafter, the most important properties of electronic wave functions are discussed: normalization, antisymmetry and inclusion of the electronic spin. This leads to the concept of Slater determinants constructed from spin orbitals. How the molecular orbitals can be calculated by means of the Hartree-Fock approach is shown for the simplest case of a closed shell state. Finally, a presentaion of the configuration interaction (CI) method which is used both for improving Hartree-Fock wave functions and for treating excited states concludes the lecture.

1 Introduction

In this lecture we will present a short introduction to the most elementary methods of wave function based quantum chemistry. We will primarily discuss the basic concepts and will not present long derivations or technical implementations in detail. The subject of this lecture is covered in all textbooks on electronic structure theory, a small selection of titles is contained in the list of references.[1-7] In particular, the presentation given in Ref. 7 is close to the one of the present lecture.

Wave function based quantum chemical methods can be characterized as being "ab initio" methods. This means that in these methods mathematical approximations to the full N-electron Schrödinger equation are constructed without the help of any adjustable parameters (except for the fundamental constants of physics) that can be fitted to reproduce experimental data. It is further characteristic for ab initio methods that they can be systematically improved towards the exact solution of the Schrödinger equation and that they possess an intrinsic criterion for the quality of the current approximation.

In the following sections we will use atomic units throughout

$$e = 1,\ m = 1,\ \hbar = 1,\ 4\pi\epsilon_0 = 1$$

Further, we will (nearly consistently) adopt the convention to use upper case letters for N-electron quantities and lower case letters for one-electron quantities. Only in some cases, when this convention too strongly contradicts the common use of symbols, we will deviate from it.

2 The Molecular Hamiltonian

Our aim is to solve the Schrödinger equation for the system under consideration (isolated atom, molecule, nanoparticle or extended system). In general, this system consists of a

certain number K of nuclei and a number N of electrons. The Hamiltonian, which determines the motion of the system, as well as its wave function will depend on the coordinates of all the nuclei and all the electrons. We will denote the coordinates of the nuclei by upper case letters $\underline{R}$ and those of the electrons by lower case letters $\underline{r}$. By underlining R and r we indicate that we consider the coordinates of all nuclei or electrons.

The Schrödinger equation for our system is given by

$$H(\underline{R},\underline{r})\Psi(\underline{R},\underline{r}) = E\Psi(\underline{R},\underline{r}) \tag{1}$$

In the simplest case, i.e. if no external electrostatic or magnetic fields are present and if we restrict the interaction between the particles to the Coulomb interaction, the molecular Hamilton operator $H(\underline{R},\underline{r})$ reads

$$H(\underline{R},\underline{r}) = T_n + T_{el} + V_{n,el} + V_{el,el} + V_{n,n} \tag{2}$$

where

$$T_n = -\frac{1}{2}\sum_{\alpha}^{K}\frac{\Delta_\alpha}{M_\alpha} \tag{3}$$

(Δ_α being the Laplace operator for the coordinates of the α-th nucleus) is the operator of the kinetic energy of the nuclei,

$$T_{el} = -\frac{1}{2}\sum_{i}^{N}\Delta_i \tag{4}$$

is the operator of the kinetic energy of the electrons,

$$V_{n,el} = -\sum_{i}^{N}\sum_{\alpha}^{K}\frac{Z_\alpha}{r_{i\alpha}} \tag{5}$$

is the Coulomb attraction between the nuclei possessing the charges Z_α and the electrons,

$$V_{el,el} = \sum_{i}^{N}\sum_{j}^{N}\frac{1}{r_{ij}} \tag{6}$$

is the Coulomb repulsion between the electrons, and

$$V_{n,n} = \sum_{\alpha}^{K}\sum_{\beta}^{L}\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \tag{7}$$

is the Coulomb repulsion between the nuclei. It must be noted that this Hamiltonian does not contain:

a) External electric or magnetic fields. It is, however, quite straightforward to include the respective terms in the Hamiltonian. One has simply to take the classical expressions for the interaction of electric or magnetic moments with the corresponding fields and to replace the formulas with their quantum mechanical equivalents.
b) Relativistic effects. The Hamiltonian given above is only valid for "slow" particles, i.e. for particles moving with a velocity much smaller than the velocity of light. This is generally sufficient for light elements, $Z < 40$, and also for the valence electrons of heavier elements. A rigorous theory of relativistic effects in quantum mechanical systems is rather complicated and beyond the scope of the present lecture.

c) Spin dependent terms. Since the Hamiltonian (Eq. (2)) does not contain any terms which depend on the spins of the nuclei or the electrons it cannot be used to describe spin properties like spin-orbit or spin-spin couplings. However, as we will see in the next sections, some spin properties are introduced indirectly by the permutation symmetry of the wave function.

3 Born-Oppenheimer Approximation

For a system with K nuclei and N-electrons, the Schrödinger equation (Eq. (1)) is an eigenvalue equation in $3K + 3N$ independent variables, the cartesian coordinates of all the particles. Since it is in general impossible to solve such a problem exactly, either analytically or numerically, it is necessary to find approximate solutions, which are accurate enough to provide useful information.

The first of such approximations, which has been proposed 1927 by Born and Oppenheimer,[8,9] consists in a separation of the motion of the light and therefore "fast" electrons from that of the "slow" nuclei. We write the total wave function $\Psi(\underline{R}, \underline{r})$ in the form of a product of an electronic wave function $\Phi_{el}(\underline{r}; \underline{R})$ and a wave function $\chi_n(\underline{R})$, which describes the motion of the nuclei:

$$\Psi(\underline{R}, \underline{r}) = \Phi_{el}(\underline{r}; \underline{R}) \cdot \chi_n(\underline{R}) \tag{8}$$

By means of this ansatz, the total Schrödinger equation (Eq. (1)) is decomposed into one equation for the electronic wave function $\Phi_{el}(\underline{r}; \underline{R})$

$$H_{el}\Phi_{el}(\underline{r}; \underline{R}) = E_{el}(\underline{R})\Phi_{el}(\underline{r}; \underline{R}) \tag{9}$$

with the electronic Hamiltonian

$$H_{el} = H - T_n = T_{el} + V_{n,el} + V_{el,el} + V_{n,n} \tag{10}$$

and one equation for the wave function $\chi_n(\underline{R})$ describing the motion of the nuclei

$$[T_n + E_{el}(\underline{R}) + C(\underline{R})]\chi_n(\underline{R}) = E\chi_n(\underline{R}) \tag{11}$$

The independent variables in the electronic wave function $\Phi_{el}(\underline{r}; \underline{R})$ are the coordinates $\underline{r}$ of the electrons; however, $\Phi_{el}(\underline{r}; \underline{R})$ depends also parametrically on the coordinates $\underline{R}$ of the nuclei, because the electronic Hamiltonian is a function of the positions $\underline{R}$ of the nuclei. That means that the electronic Schrödinger equation has to be solved for a given nuclear geometry ("clamped nuclei approximation"). The consequence is that the electronic energy, i.e. the eigenvalue $E_{el}(\underline{R})$ of the electronic Schrödinger equation (Eq. (9)), is not a constant, but depends also on the nuclear geometry. This geometry dependent electronic energy $E_{el}(\underline{R})$ plays the role of the potential energy in the Schrödinger equation (Eq. (11)) for the nuclear motion. Its is therefore generally termed "potential energy surface" (PES). The energy E in Eq. (11), on the other hand, is a pure number, the energy eigenvalue of the total Schrödinger equation (Eq. (1)).

It has to be noted that concepts such as "potential energy curve" or "potential energy surface" $E(\underline{R})$ as well as geometrical structures etc. are only defined within the Born-Oppenheimer approximation!

Comments:

a) One has also tried an ansatz similar to Eq. (8) in which the electronic wave function is independent of the nuclear geometry $\underline{R}$, the so-called "crude adiabatic approximation". But this scheme is so inaccurate that it is completely useless.

b) The term $C(\underline{R})$ in Eq. (11) is called the "adiabatic diagonal correction". It is an operator acting on the nuclear wave function $\chi_n(\underline{R})$. Its explicit form is given by

$$C(\underline{R}) = \int \Phi^{\star}_{el}(\underline{r};\underline{R}) T_n \Phi_{el}(\underline{r};\underline{R}) d\underline{r} - \sum_{\alpha} \frac{1}{M_\alpha} \int \Phi^{\star}_{el}(\underline{r};\underline{R}) \nabla_\alpha \Phi_{el}(\underline{r};\underline{R}) d\underline{r} \cdot \nabla_\alpha \tag{12}$$

Because of the nuclear masses in the denominators in Eq. (12) this term is generally quite small and is mostly neglected altogether. Sometimes one distinguishes between the "Born-Oppenheimer" approximation, if $C(\underline{R})$ is neglected, and the "adiabatic approximation" if it is included.

c) In most cases the Born-Oppenheimer approximation is a very good approximation. Generally, it is only necessary to go beyond it in cases of degeneracies or near degeneracies or at very high energies for the nuclear motion.

d) Finally, if one has to go beyond the Born-Oppenheimer approximation, one can extend the ansatz (Eq. (8)) by using a linear combination of products of electronic and nuclear wave functions.

4 Requirements for the Electronic Wave Function

In the following, we will stay within the Born-Oppenheimer approximation and will only be concerned with the electronic Schrödinger equation (Eq. (9)). For simplicity, we will drop the subscript "el" and the nuclear coordinates $\underline{R}$ from $\Phi_{el}(\underline{r};\underline{R})$.

A wave function which shall be used for describing the electronic structure of the system under consideration has to satisfy three requirements, in addition to being an approximate or exact solution of the electronic Schrödinger equation (Eq. (9)).

a) Normalization. As for all quantum mechanical wave functions describing stationary states we will assume that $\Phi(\underline{r})$ is normalized to unity, i.e.

$$\int \Phi^{\star}(\underline{r}) \Phi(\underline{r}) d\underline{r} = 1 \tag{13}$$

where the integration is to be performed over the coordinates of all N electrons. The condition (Eq. (13)) simply means that the probability for finding the system somewhere in space is unity.

b) Antisymmetry with respect to the permutation of two electrons. Since electrons are fermions, the only solutions of the electronic Schrödinger equation, which can be used for describing electronic systems, have to be antisymmetric with respect to a permutation of any two electrons in the system. Mathematically speaking, only wave functions which belong to the totally antisymmetric representation of the permutation group of N electrons are allowed to describe N-electron systems.

If we denote a permutation of the electrons i and j by the operator P_{ij}, the antisymmetry requirement can be formulated as

$$P_{ij}\Phi(1,...,i,...,j,...,N) = \Phi(1,...,j,...,i,...,N) = -\Phi(1,...,i,...,j,...,N) \tag{14}$$

where we have simply indicated the order of the electrons by noting their serial numbers.

More generally, one can define an "antisymmetrizer" $\mathcal{A}$ which generates a fully antisymmetric wave function from any trial wave function $\tilde{\Phi}$

$$\mathcal{A} = \mathcal{N} \sum_P \epsilon_p P \tag{15}$$

where $\mathcal{N}$ is a normalization constant and the sum runs over all permutations P of the permutation group of N elements, with ϵ_p being the parity of the permutation P.

c) Electronic spin. Since the electronic Hamiltonian (Eq. (10)) does not contain any spin operators, it does commute with the operators S_z and S^2 of the z-component and the square of the total electronic spin

$$[H, S_z] = 0, [H, S^2] = 0 \tag{16}$$

where S_z and S^2 are the N-electron spin operators

$$S_z = \sum_i^N s_{z_i}, S^2 = \sum_i^N s_i^2 \tag{17}$$

This means that electronic wave functions have to be eigenfunctions of S_z and S^2 with the eigenvalues M_S and $S(S+1)$.

A rigorous quantum mechanical treatment of one-electron with spin is only possible by means of the Dirac equation in which four-component or at least two-component one-electron wave functions (spinors) have to be used. Such a treatment is beyond the scope of this lecture. Here, we use a simplified scheme by representing the wave function of an electron with spin by a product

$$\psi(x, y, z, s) = \phi(x, y, z) \cdot \eta(s) \tag{18}$$

of a spatial part $\phi(x, y, z)$ which depends on the three spatial coordinates x, y, z and a spin function $\eta(s)$ which depends on the spin of the electron. There are only two possible spin functions $\eta(s)$ which are commonly denoted by "α" and "β" and which can be chosen to be orthogonal. In the quantum chemical literature the beta-spin is generally denoted by a bar above the orbital while the alpha-spin is not indicated, i.e. the one-electron wave functions with spin are

$$\phi(x, y, z) \cdot \alpha = \phi \tag{19}$$

$$\phi(x, y, z) \cdot \beta = \bar{\phi} \tag{20}$$

We will denote the one-electron wave functions with spin, $\psi(x, y, z, s)$ as given in Eq. (18), as "spin orbitals", while the spinfree one-electron wave functions $\phi(x, y, z)$ are simply called "orbitals".

In the following we will try to construct approximate N-electron wave functions. Whenever possible, they should satisfy the above mentioned requirements. There is no problem with the normalization. The antisymmetry can also be achieved, at least formally, by applying the antisymmetrizer (Eq. (15)). Finally, the electronic spin is taken care of at the one-electron level by using spin orbitals instead of pure spatial orbitals. However, it is generally difficult to construct N-electron spin eigenfunctions. We will see in the next section that in most cases it is quite easy to obtain eigenfunctions of S_z (simply because this is a sum of one-electron operators), but not for S^2.

5 Slater Determinants

A closer inspection of the electronic Hamiltonian (Eq. (10)) shows that it contains one-electron terms, i.e. terms that depend only on the coordinates of one electron, two-electron terms, and the nuclear repulsion $V_{n,n}$ which is independent of the electron coordinates

$$H = \sum_i h(i) + \sum_{i<j} g(ij) + V_{n,n} \tag{21}$$

$$h(i) = -\frac{1}{2}\Delta_i - \sum_\alpha^K \frac{Z_\alpha}{r_{i\alpha}}, \quad g(ij) = \frac{1}{r_{ij}} \tag{22}$$

with $V_{n,n}$ given by Eq. (7).

Since $V_{n,n}$ is just a constant with respect to the electronic coordinates, it causes no problems. If the two-electron terms $g(ij)$ were absent, H would be a sum of terms each depending only on the coordinates of one electron. Then H would be separable: its eigenfunctions would be just products of eigenfunctions of the one-particle Hamiltonian h and its eigenvalues sums of eigenvalues of h. Unfortunately, H contains the two-electron repulsion terms $g(ij)$, and, also unfortunately, they are by no means small and cannot be simply neglected.

Nevertheless, we start by constructing trial wave functions as products of one-electron wave functions

$$\Phi(1, ..., N) = \psi_a(1) \cdot \psi_b(2) \cdot ... \cdot \psi_N(N) \tag{23}$$

Here, the serial number "1" again stands for the (space and spin) coordinates of electron number 1, etc. In order to account for the spins of the electrons, the one-electron wave functions $\psi_a(1)$ etc. in the product (Eq. (23)) are chosen to be the spin orbitals given in Eq. (18). Eq. (23) is interpreted by saying that the first electron is "occupying" the spin orbital ψ_a, the second electron the spin orbital ψ_b and so on.

Now, the product (Eq. (23)) does not possess the required antisymmetry property, therefore we have to apply the antisymmetrizer $\mathcal{A}$ (Eq. (15)) and obtain

$$\Phi(1, ..., N) = \mathcal{A}[\psi_a(1) \cdot \psi_b(2) \cdot ... \cdot \psi_N(N)] \tag{24}$$

Since the antisymmetrizer (Eq. (15)) is nothing else than an operator generating a determinant out of a simple product we can write the trial N-electron wave function in the form of a determinant

$$\Phi(1, ..., N) = |\psi_a(1)\psi_b(2)...\psi_N(N)| \tag{25}$$

with $|...|$ being the usual notation for a determinant, but includes the normalization constant $\mathcal{N}$. Eq. (25) is indeed a determinant, the rows of which are numbered by the electrons and the columns by the occupied spin orbitals (or the other way round). Because of the antisymmetry of determinants, the Pauli principle is automatically satisfied; Eq. (25) vanishes if two of the occupied spin orbitals are identical. Such determinants, in which the elements are not numbers, but orbitals or spin orbitals, are called "Slater determinants".[10] Though the form of our trial wave function (Eq. (25)) looks quite simple, one should not forget that it is a linear combination of product wave functions with as many as $N!$ terms.

In most cases it is assumed that the (spatial) orbitals ϕ_a form an orthonormal set, i.e. that the overlap integral between two orbitals is equal to the Kronecker δ

$$(\phi_a|\phi_b) = \int \phi_a^\star \phi_b dr = \delta_{ab} \tag{26}$$

where the integration is over the three spatial coordinates of the electron. Because of the orthogonality of the spin functions α and β, the spin orbitals ψ_a form an orthonormal set as well

$$(\psi_a|\psi_b) = \int \psi_a^\star \psi_b d\tau = \delta_{ab} \tag{27}$$

where the integration $d\tau$ also includes summation over the two spin orientations. In this case the normalization constant $\mathcal{N}$ in Eq. (25) is given by $1/\sqrt{(N!)}$. In principle, it is not necessary to choose orthonormal orbitals ϕ_a, however, all formulas become much simpler if Eq. (26) and Eq. (27) are satisfied.

N-electron wave functions in the form of Slater determinants possess several important properties:

a) By construction, they satisfy the antisymmetry property and the Pauli principle.
b) They offer an easy interpretation, since nothing seems more natural than the idea that a certain electron is attributed to a certain one-electron function or, stated differently, that an electron is occupying a certain orbital and possesses either the spin α or β. The molecular orbital theory of chemical bonding is entirely based on this interpretation. Of course, other forms of N-electron wave functions have also been proposed, e.g. in the so-called "valence bond theory", but such a simple and natural interpretation is lacking most of them.
c) Whenever spin orbitals of the form (18)-(20) are used, Slater determinants are eigenfunctions of the N-electron spin operator S_z with an eigenvalue M_S equal to one-half of the difference between the number of α and β electrons:

$$S_z\Phi = M_S\Phi, M_S = \frac{1}{2}(N_\alpha - N_\beta) \tag{28}$$

However, except for a few simple cases, Slater determinants are not eigenfunctions of the N-electron spin operator S^2. One of the exceptions is the situation of a closed shell system, in which there is an even number of electrons $N = 2n$ and exactly n spatial orbitals are doubly occupied. Fortunately, the stable ground states of most molecules belong to this case which will be treated in more detail in the next section. Whenever a single Slater determinant is not an eigenfunction of S^2, one can construct eigenfunctions as linear combinations of Slater determinants, in which the same (spatial) orbitals are occupied, but with different spin orientations. Such linear combinations have coefficients which are fixed by spin or spatial symmetry and are called "configuration state functions" (CSFs).
d) In many applications, e.g. in Hartree-Fock theory or in configuration interaction, one needs matrix elements of the N-electron Hamiltonian H or other N-electron operators between different Slater determinants. Though one Slater determinant consists of as many as $N!$ products of N spin orbitals, the construction of such matrix elements is straightforward and leads to rather simple formulas, in particular if the spatial orbitals ϕ_a are chosen orthonormal (Eq. (26)).

We will not report the general formulas for these matrix elements, but will present only two special cases, namely the normalization integral and the energy expectation value for the determinant

$$\Phi = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 ... \phi_n \bar{\phi}_n| \tag{29}$$

describing a closed shell system with an even number of electrons, $N = 2n$, and n (spatial) orbitals ϕ_i are doubly occupied. If one assumes that the orbitals ϕ_i are orthonormal, one can derive

$$(\Phi|\Phi) = 1 \tag{30}$$

$$(\Phi|H|\Phi) = \sum_{i=1}^{n} 2(i|h|i) + \sum_{i,j=1}^{n} [2(ii|jj) - (ij|ji)] \tag{31}$$

where the following one- and two-electron integrals occur: One-electron integral

$$(i|h|i) = \int \phi_i^\star(1) h(1) \phi_i(1) dr_1 \tag{32}$$

two-electron Coulomb-integral

$$(ii|jj) = \int \phi_i^\star(1) \phi_i(1) \frac{1}{r_{12}} \phi_j^\star(2) \phi_j(2) dr_1 dr_2 \tag{33}$$

and two-electron exchange-integral

$$(ij|ji) = \int \phi_i^\star(1) \phi_j(1) \frac{1}{r_{12}} \phi_j^\star(2) \phi_i(2) dr_1 dr_2 \tag{34}$$

The N-electron expectation value (Eq. (31)) contains, as expected, the one-electron expectation values $(i|h|i)$ for all occupied orbitals and the Coulomb interaction $(ii|jj)$ between the occupied orbitals. In addition, there is a "new" term, the exchange interaction $(ij|ji)$. While the Coulomb-integral $(ii|jj)$ corresponds exactly to the classical Coulomb interaction between two charge distributions $\phi_i^\star \phi_i$ and $\phi_j^\star \phi_j$, the exchange interaction has no classical analogue and is a consequence of the antisymmetry requirement to the quantum mechanical wave function Φ.

Formulas for the matrix elements of the overlap matrix and of the N-electron Hamiltonian, between different Slater determinants Φ_I and Φ_J, can be generated as well.[11] Such formulas are needed in the method of configuration interaction as well as in all other post Hartree-Fock approaches.

6 Hartree-Fock Theory for Closed Shell States

Let us again consider an electronic system containing an even number of electrons, $N = 2n$. As mentioned above, this situation is realized for most ground states of stable molecules or periodic systems. In such cases, a one-determinant wave function of the form

$$\Phi_{SCF} = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 ... \phi_n \bar{\phi}_n| \tag{35}$$

in which n (spatial) orbitals ϕ_i are occupied by two electrons each, once with α and once with β spin, will be in general a good approximation to the true ground state wave function

of the N-electron Hamiltonian. It can be shown that such a determinant is an eigenfunction of both S_z and S^2 with the eigenvalues $M_S = 0$ and $S(S+1) = 0$, i.e. it is a pure singlet state with a spin quantum number $S = 0$. The Hartree-Fock or self-consistent field (SCF) approach consists essentially in making the ansatz (Eq. (35)) for the N-electron wave function of the system under consideration.[12,13]

The orbitals ϕ_i which are occupied in Φ_{SCF} are in general not known, but have yet to be determined. One choice could be the eigenfunctions of the one-particle Hamiltonian h (Eq. (22)). But this would mean to neglect the electron-electron repulsion entirely which yields too poor an approximation. In order do determine a reasonable set of orbitals one has to apply the variation principle to the wave function (Eq. (35)) and to vary the energy expectation value calculated with Φ_{SCF} as a functional of the occupied orbitals ϕ_i. The formula for this expectation value is given in Eq. (31), however, this simple formula is only valid if the occupied orbitals form an orthonormal set. That means that the energy expectation value has to be varied under the constraint that the orbitals remain orthonormal during the variation. This can be most easily achieved by using the method of the Lagrangean multipliers.

Therefore, we have to search for the minimum of the functional

$$\mathcal{J}[\phi] = \sum_{i=1}^{n} 2(i|h|i) + \sum_{i,j=1}^{n} [2(ii|jj) - (ij|ji)] - \sum_{i,j=1}^{n} 2\lambda_{ij}[(\phi_i|\phi_j) - \delta_{ij}] \tag{36}$$

by varying the orbitals ϕ_i. The coefficients λ_{ij} are the unknown Lagrangean multipliers. Performing this variation one arrives at the following one-particle eigenvalue equation

$$[h + \sum_{j}^{occ}(2J_j - K_j)]\phi_i = \sum_{j}^{n} \lambda_{ij}\phi_j \qquad \text{for each } \phi_i \tag{37}$$

In this equation there are two operators describing the electron-electron interaction: The "Coulomb operator" J_j whose action on an arbitrary one-electron wave function ω is given by

$$J_j(1)\omega(1) = \int \phi_j^\star(2)\phi_j(2)\frac{1}{r_{12}}dr_2 \cdot \omega(1) \tag{38}$$

and the "exchange operator" K_j

$$K_j(1)\omega(1) = \int \phi_j^\star(2)\omega(2)\frac{1}{r_{12}}dr_2 \cdot \phi_j(1) \tag{39}$$

The Coulomb operator J_j describes the classical Coulomb repulsion that the electron number 2 occupying the orbital ϕ_j is exercising on the electron number 1 in the orbital ω, while the non-classical exchange operator is again the consequence of the antisymmetry of the N-electron wave function. It has to be noted that the Coulomb operator is a local operator, while the exchange operator is a non-local integral operator containing the wave function ω in the integral kernel. That means that for calculating the action of this operator onto a wave function ω at a certain point in space one has to know the function ω everywhere in space. Of course, this property renders the evaluation of exchange terms more complicated than that of Coulomb terms.

The sum over j on the l.h.s. of Eq. (37) runs over all n orbitals which are occupied in the SCF wave function Φ_{SCF}; the sum on the r.h.s. of Eq. (37) involves the still unknown Lagrangean multipliers λ_{ij}.

Eq. (37) can be further simplified by noting that the SCF wave function Φ_{SCF} Eq. (35), being a determinant, is invariant with respect to unitary transformations among the occupied orbitals ϕ_i. This freedom can be used in order to bring the matrix λ_{ij} of the Lagrangean multipliers to a diagonal form. If we denote its diagonal elements by ϵ_i and introduce the "Fock operator" F by means of

$$F = h + \sum_{j}^{occ}(2J_j - K_j) \tag{40}$$

the one-electron equation determining the orbitals ϕ_i reads

$$F\phi_i = \epsilon_i\phi_i \tag{41}$$

This is the famous Hartree-Fock equation, which plays the role of a one-electron Schrödinger equation for the orbitals ϕ_i. Its main properties can be briefly characterized as follows:

a) Eq. (37) or Eq. (41) is an integro-differential equation, since the kinetic energy operator contained in h involves differentiation and the exchange operators K_j are integral operators. Eq. (41) has the form of an eigenvalue equation, similar to the original N-electron Schrödinger equation (Eq. (9)).

b) Since the Coulomb and exchange operators in the Fock operator F (Eq. (40)) have to be constructed from the orbitals ϕ_i which are yet to be determined by solving the Hartree-Fock equation (Eq. (41)), iterative schemes are necessary. Generally, one starts with some guess, $\phi_i^{(0)}$, constructs the operators $J_j^{(0)}$, $K_j^{(0)}$, and $F^{(0)}$ (Eqs. (38)-(40)) with them and solves Eq. (41). This will yield a new set of orbitals and orbital energies, $\phi_i^{(1)}$ and $\epsilon_i^{(1)}$. From them, a new Fock operator $F^{(1)}$ is constructed. Then again Eq. (41) can be solved, yielding the next set of orbitals and orbital energies, and so on. This procedure is repeated till "self-consistency" is reached, i.e. till the orbitals used for constructing the Fock operator are identical with the ones obtained by the solution of Eq. (41). Because of this self-consistency requirement, the Hartree-Fock method has the alternative name "self-consistent field" (SCF) method. Therefore we have already used the subscript "SCF" for the wave function (Eq. (35)).

c) The Hartree-Fock equation (Eq. (41)) has infinitely many solutions, ϕ_i and ϵ_i, or rather a finite number of M solutions if one is working in a finite space of M one-electron basis functions (see next section). The ground state of the N-electron system is obtained if the energetically lowest Hartree-Fock orbitals are occupied in Φ_{SCF} (Aufbau principle). Generally one distinguishes between
   - occupied orbitals ϕ_i, $i = 1, ..., n$, i.e. those orbitals occupied in Φ_{SCF} which are used to construct the Coulomb and exchange operators, and
   - virtual orbitals ϕ_i, $i > n$, which are not occupied in Φ_{SCF}. Strictly speaking, the virtual orbitals are not "optimized", since the energy expectation value (Eq. (31)) does not depend on them at all. They are, however, frequently used for electronically excited states as well as in CI approaches (see Section 8).

d) The eigenvalues ϵ_i of the Hartree-Fock equation are called "orbital energies". In general, they are negative for occupied (bound) orbitals and positive for virtual (continuum) orbitals. The orbital energies of the occupied orbitals can be identified with the

ionization potentials of the system

$$\epsilon_i = -IP(i) \tag{42}$$

(Koopmans' theorem).[14] Eq. (42) states that the orbital energy ϵ_i of the i-th occupied orbital is equal to the negative value of the energy necessary to remove one-electron from orbital ϕ_i. However, this is only an approximation because in deriving the theorem it has been assumed that the orbitals do not change (relax) after ionization. The accuracy of Koopmans' theorem is in the order of 0.5 - 2.0 eV for valence orbitals, for core orbitals the errors are much larger.

e) After the Hartree-Fock equations have been solved and the Hartree-Fock orbitals have been obtained, one has to evaluate the Hartree-Fock energy E_{SCF} as the expectation value of the N-electron Hamiltonian, calculated with Φ_{SCF} (Eq. (35)). In contrast to the naive interpretation, E_{SCF} is not equal to the sum of the orbital energies of the occupied orbitals, since in this sum the electron-electron interaction is double-counted. Instead one finds

$$E_{SCF} = \sum_{i}^{n} [(i|h|i) + \epsilon_i] \tag{43}$$

The Hartree-Fock theory presented so far is only applicable to closed shell states which can be described by a wave function of the type of Eq. (35). It is, however, possible to extend this procedure to open shell systems, but the formalism is more complicated than for closed shell states. A detailed discussion is beyond the aim of this lecture; we will only give the acronyms for the most widely used variants of open shell Hartree-Fock theory: ROHF (restricted open shell Hartree-Fock) and UHF (unrestricted Hartree-Fock) for simpler cases where a one-determinant open shell wave function can be used, and MC-SCF (multi-configuration SCF) and CASSCF (complete active space SCF) for cases in which a multi-determinant wave function is necessary.

7 Roothaan SCF

Though the Hartree-Fock theory has been formulated in the early 1930ths, for a long time numerical calculations could only be performed for atoms. The reason is that Eq. (41) is an integro-differential equation in the 3D space which could not be solved by e.g. finite difference methods. Numerical solutions were only possible for atoms where one can separate the angular from the radial part and is left with 1D radial equations.

The breakthrough for molecular calculations came in 1951 when Hall[15] and Roothaan[16] independently proposed to expand the Hartree-Fock orbitals into a set of atom centered basis functions. At first, atomic orbitals were used for that purpose,[17] but it turned out that the calculation of the necessary one- and two-electron integrals was much too difficult and time consuming. The proposal of Boys[18] to use Gaussian functions instead opened the way to the field of electronic structure calculations for molecules.

The idea of Roothaan is to expand the unknown Hartree-Fock orbitals ϕ_i into a finite set of M known functions χ_ν, called "basis functions"

$$\phi_i = \sum_{\nu=1}^{M} c_{i\nu} \chi_\nu \tag{44}$$

Now, the coefficients $c_{i\nu}$ determine the orbitals ϕ_i and have to be calculated. One can either use the variation principle again and vary the energy expectation with respect to these coefficients or one can project the Hartree-Fock equation (Eq. (41)) onto the basis functions χ_ν. In both cases one obtains a matrix eigenvalue equation of the form

$$\sum_{\nu}^{M} F_{\mu\nu} c_{i\nu} = \epsilon_i \sum_{\nu}^{M} S_{\mu\nu} c_{i\nu}, \qquad \text{for all } \mu = 1, .., M \tag{45}$$

or in a matrix notation

$$\underline{\underline{F}} \cdot \underline{c}_i = \epsilon_i \underline{\underline{S}} \cdot \underline{c}_i \tag{46}$$

where $\underline{\underline{F}}$ and $\underline{\underline{S}}$ are the Fock and overlap matrices and $\underline{c}_i$ the coefficient vectors. The matrix elements of the overlap matrix are defined as in Eq. (26)

$$S_{\mu\nu} = (\mu|\nu) = (\chi_\mu|\chi_\nu) = \int \chi_\mu^\star \chi_\nu dr \tag{47}$$

In general, the basis functions cannot be chosen in such a way that S is the unit matrix. The Fock matrix is constructed from one- and two-electron integrals

$$F_{\mu\nu} = (\mu|h|\nu) + \sum_{j} \sum_{\rho,\sigma} c_{j\rho} c_{j\sigma} [2(\rho\sigma|\mu\nu) - (\rho\nu|\mu\sigma)] \tag{48}$$

with the matrix elements of the one-electron Hamiltonian (one-electron integrals) are given by

$$(\mu|h|\nu) = (\chi_\mu|h|\chi_\nu) = \int \chi_\mu^\star h \chi_\nu dr \tag{49}$$

and the two-electron integrals by

$$(\rho\sigma|\mu\nu) = \int \chi_\rho^\star(1) \chi_\sigma(1) \frac{1}{r_{12}} \chi_\mu^\star(2) \chi_\nu(2) dr_1 dr_2 \tag{50}$$

The solution of the Hartree-Fock equation (Eq. (41)) is now achieved by the solution of the matrix eigenvalue equation (Eq. (45)), which yields the orbital energies ϵ_i and the coefficient vectors $c_{i\nu}$. Obviously, the "analytic" form of Eq. (41) and the "algebraic" form of Eq. (45) of the Hartree-Fock equation are only equivalent if $M \to \infty$, i.e. if a complete one-electron basis set is employed ("SCF limit").

Of course, the necessary numerical effort as well as the accuracy which can be achieved depend crucially on the quality and the size of the basis set χ_ν. The numerical effort is easy to estimate: There are M^4 two-electron integrals $(\mu\nu|\rho\sigma)$ for a basis with M basis functions χ_ν and the solution of the Hartree-Fock equation (45) requires the diagonalization of a M-dimensional matrix which is a M^3 step. On the other hand, the design of good basis sets requires a lot of experience and is by no means trivial. Fortunately, reasonable basis sets, spanning a wide range from rather poor and fast to very accurate and time consuming, have been determined during the last 50 years for all atoms and most applications. They are available in the commercial program packages.

Today, one can distinguish between two technical implementations of the Roothaan SCF procedure:

a) Conventional SCF: One chooses a basis set, calculates all one- and two-electron integrals $(\mu|\nu)$, $(\mu|h|\nu)$, $(\mu\nu|\rho\sigma)$ and stores them on a peripheral storage device (disk). All integrals are read in and processed in every SCF iteration. Since I/O is slow compared to CPU in modern computers, this method is strongly I/O bound. The large number of two-electron integrals requires much peripheral space. The largest basis sets that can be handled this way can contain about 800-1200 basis functions.

b) Direct SCF[19]: The two-electron integrals $(\mu\nu|\rho\sigma)$ are not calculated and stored prior to the SCF iterations, but are recalculated in each iteration. Of course, only those integrals are calculated which are really needed. For instance, Eq. ((48) shows that it is not the integral $(\mu\nu|\rho\sigma)$ itself that is needed, but always a combination like

$$c_{j\rho}c_{j\sigma}[2(\rho\sigma|\mu\nu) - (\rho\nu|\mu\sigma)] \tag{51}$$

i.e. a product of a density matrix element $c_{j\rho}c_{j\sigma}$ and a combination of integrals. That means, it is not necessary to calculate the integral if the density matrix element is too small or does not change from one iteration to the next ("prescreening" and "updating"). This way one can use basis sets of several thousand functions without needing much peripheral space. With efficient prescreening techniques the necessary computer times are not larger than for the conventional procedure.

8 Configuration Interaction

The Hartree-Fock method yields, even in favorable cases and if large one-particle basis sets are employed, only an approximation to the exact solution of the electronic Schrödinger equation (9). In many cases, in particular when accurate results are to be obtained, one has to go beyond the Hartree-Fock method.

In general, we denote all effects beyond the Hartree-Fock level as "correlation" effects. We will especially define the correlation energy of a system as the difference between the "exact" energy eigenvalue of the N-electron Hamiltonian and the SCF energy:

$$E_{corr} = E - E_{SCF} \tag{52}$$

The conceptually simplest method for accounting for correlation effects is the method of configuration interaction (CI). The main idea is based on the following lemma (expansion theorem): Let $\phi_i, i = 1, ..., \infty$ be a complete basis of the one-particle Hilbert space. Then it can be proven that all N-electron Slater determinants

$$\Phi_I(1, ..., N) = |\phi_{I1}(1)\phi_{I2}(2)...\phi_{IN}(N)| \tag{53}$$

which can be constructed by placing the N electrons into N of these orbitals in all possible ways, span the full antisymmetric N-particle Hilbert space. That means that any N-electron wave function can be expanded into the set of determinants $\Phi_I(1, ..., N)$ (Eq. (53)). This holds, of course, also for the eigenfunctions of the N-electron Hamiltonian, i.e. we can make the following ansatz for them

$$\Psi_i(1, ..., N) = \sum_I C_{iI}\Phi_I(1, ..., N) \tag{54}$$

where we have denoted the eigenfunctions by Ψ_i in order to distinguish them from the Slater determinants Φ_I. It has to be stressed, that the expansion (Eq. (54)) holds for any

complete set of one-electron functions, i.e. for any basis of the one-particle Hilbert space, but the expansion coefficients C_{iI} will of course depend on the choice of the basis.

The CI method uses this lemma in the following manner: As usual, one selects a set of atomic basis functions, $\chi_\mu, \mu = 1, ..., M$. By means of a Hartree-Fock calculation or simply by an orthogonalization procedure a set of orthonormal molecular orbitals $\phi_i, i = 1, ..., M$ is constructed as linear combinations of the χ_μ. By combining the spatial orbitals with the spin functions α and β (Eqs. (19),(20)) one obtains $2M$ spin orbitals ψ_i. They are used to build up Slater determinants in the form indicated in Eq. (53) or configuration state functions (CSFs or simply "configurations") as fixed linear combinations of such determinants. And finally, the eigenfunctions of the N-particle Hamiltonian are expanded into these determinants as shown in Eq. (54). Of course, in real calculations one can only use a finite number M of atomic basis functions and therefore the Φ_I span only a finite subspace of the full N-particle Hilbert space.

For the determination of the expansion coefficients C_{iI} (CI coefficients) the variation principle is invoked again: The expectation value of the N-electron Hamiltonian, calculated with the wave function Ψ_i, has to be minimized as a function of the C_{iI}. Since Ψ_i depends only linearly on the parameters C_{iI}, the application of the variation principle is particularly simple ("linear" or "Ritz" variation principle) and leads to a set of linear equations

$$\sum_J (H_{IJ} - ES_{IJ})C_J = 0, \qquad \text{for all I} \tag{55}$$

The quantities H_{IJ} and S_{IJ} in these equations are the matrix elements of the N-particle Hamiltonian and the overlap matrix calculated with the Slater determinants Φ_I and Φ_J

$$H_{IJ} = (\Phi_I|H|\Phi_J), \quad S_{IJ} = (\Phi_I|\Phi_J) \tag{56}$$

They can be easily evaluated (see Section 5) as long as the orbitals ϕ_i form an orthonormal set.

Eq. (55) is a set of homogeneous linear equations which has only non-trivial solutions if the determinant of the coefficient matrix vanishes. This leads to the secular equation

$$|H_{IJ} - ES_{IJ}| = 0 \tag{57}$$

This is an algebraic equation of the order of the dimension, P say, of the matrices H_{IJ} and S_{IJ}. Its solutions are the eigenvalues E_i and the eigenvectors C_{iI} of the electronic N-particle Hamiltonian, projected onto the finite, P-dimensional N-particle Hilbert space spanned by the Φ_I. Of course, one will obtain exactly P eigenvalues and eigenvectors.

Solving the secular equations (55) is equivalent to diagonalizing the matrix H_{IJ} with the metric S_{IJ}.

Though the concept as well as the numerical implementation of the CI approach are extremely simple, the method has one decisive disadvantage: The number of possible determinants Φ_I is extremely large, even for a small number N of electrons and a small size M of the atomic basis set. Though many methods have been designed and tested during the last 40 years, both for an efficient evaluation of the matrix elements H_{IJ} and S_{IJ} and for diagonalizing very large matrices, the CI problem is still not solved.

Similar to the Hartree-Fock-Roothaan approach we can distinguish between two technical implementations of the CI method: In the "conventional" scheme, the P^2 matrix elements H_{IJ} (or the matrix element formulas) are calculated once and stored on a peripheral storage device ("formula tape"), before they are processed in the iterations needed to

diagonalize H_{IJ}. For large CI dimensions P, the formula tape is getting extremely lengthy. Therefore, modern CI techniques prefer the "direct" approach, in which only those matrix elements H_{IJ} are calculated in each iteration which are needed to generate a correction vector

$$\sigma_I^{(n+1)} = \sum_J \frac{H_{IJ}}{H_{II} - E^{(n)}} C_J^{(n)} \tag{58}$$

to the CI vector $C_I^{(n)}$ with the energy $E^{(n]}$ of the preceding iteration. This way it is possible to treat CI problems with 10^5 to 10^9 determinants.

At present, CI type methods are used for several purposes:

1) Full CI
   This seems to the most straightforward scheme: As described above, one selects a finite number M of atomic basis functions, orthogonalizes them (this is only a technical step in order to be able to use simpler formulas for the matrix elements H_{IJ} and S_{IJ}), constructs all possible determinants Φ_I (maybe CSFs, adapted to the spin and spatial symmetry of the system under consideration instead of determinants), and diagonalizes H_{IJ}. As indicated above, this is only possible for small systems and small atomic basis sets. Such calculations serve primarily as benchmarks for testing the quality of approximate schemes (truncated CI, coupled-cluster methods and so on).
2) Truncated CI
   Most CI treatments are aiming at calculating correlation effects for the electronic ground state of the system. For such a purpose one generally starts from the Hartree-Fock wave function which is a good zeroth order approximation and calculates corrections to it. Full CI calculations make no sense for such cases since the vast majority of the configurations (or determinants) do not contribute at all to the wave function or the correlation energy. Rather, one has to try to select the "important" configurations and discard the unimportant ones.

   In general, this is done in the following way (for the case of a closed shell ground state): One starts from a "reference" determinant, mostly the SCF wave function as given in Eq. (35)

$$\Phi_{SCF} = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 ... \phi_n \bar{\phi}_n| \tag{59}$$

   Then one defines singly, doubly, triply, ... excited determinants, in which one, two, three,... of the spin orbitals occupied in Φ_{SCF} are replaced by virtual orbitals. If we denote the occupied orbitals by ϕ_i and ϕ_j and the virtual orbitals by ϕ_a and ϕ_b we have

   Singles (singly excited determinants)

$$\Phi(i \to a) = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 ... \phi_a \bar{\phi}_i ... \phi_n \bar{\phi}_n| \tag{60}$$

   and similarly by replacing $\bar{\phi}_i$ with $\bar{\phi}_a$.

   Doubles (doubly excited determinants)

$$\Phi(ij \to ab) = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 ... \phi_a \bar{\phi}_i ... \phi_b \bar{\phi}_j ... \phi_n \bar{\phi}_n| \tag{61}$$

   Triples and higher excited determinants are defined in an analogous way. The ansatz for the CI wave function reads

$$\Psi_{CI} = \Phi_{SCF} + \sum_{i,a} C(i \to a)\Phi(i \to a) + \sum_{ij,ab} C(ij \to ab)\Phi(ij \to ab) + ... \quad (62)$$

CI expansions truncated after the singles, doubles, triples, ... are called CIS, CISD, CISDT, ... expansions.

If one is interested in correlation effects for the electronic ground state, only the lowest root of the corresponding secular problem is calculated and analyzed. The "excited" determinants, or better "substituted" determinants, serve only for improving the description of the ground state and do not describe spectroscopically excited states.

If SCF orbitals are used in the CI, as in Eqs. (59)-(62), one can show

$$(\Phi_{SCF}|H|\Phi(i \to a)) = 0 \quad (63)$$

(Brillouin theorem). Similarly, all matrix elements of H between Φ_{SCF} and triples or higher excited determinants are zero, since H contains only one- and two-electron operators. That means that in first order only the doubles contribute to the correlation effects. In higher orders, also the singles, triples,... do contribute, but their contributions are rather small. Therefore, in many applications truncated CI-expansions are used, the most popular approach is CISD. (The singles could be discarded as well, but their number is so small that they are mostly included.)

The problem with the CISD approach is that it is not size consistent. This disadvantage is remedied by means of the "coupled-cluster" approaches which enable at present the most accurate electronic structure calculations, at least for small systems.

3) CIS
The most widely used method for calculating properties of electronically excited states is CIS (CI truncated to singles). Again, one starts from the Hartree-Fock wave function (Eq. (58)) of the corresponding electronic ground state and performs a CI calculation in which all single excitations from all occupied into all virtual orbitals are included:

$$\Psi_{CIS} = \Phi_{SCF} + \sum_{i,a} C(i \to a)\Phi(i \to a) \quad (64)$$

In contrast to the CISD approach designed for calculating correlation energies for ground states, now, the higher roots of the secular equations are used as approximations for singly excited electronic states. In this way, one can obtain a reasonably accurate description of the optical spectrum of the system.

4) Multi-reference CI (MR-CI)
In many cases, in particular in open shell systems, for excited states, or in cases of degeneracies or near degeneracies, a one-determinant Hartree-Fock wave function is not a good description, i.e. not a good zeroth order wave function, for the state under consideration. In such cases, one is forced to start from a multi-reference wave function (e.g. MC-SCF = multi configuration SCF or CASSCF = complete active space SCF) and continue with a CI on top of this reference.

Here is not enough place to go into more detail concerning the different CI versions or the other post-Hartree-Fock methods, like coupled-cluster approaches and perturbation theory. The reader is referred to the textbooks on electronic structure theory, in particular to the Ref. 5 and 7.

Exercises and Problems

1) Derive Eq. (12) using Eqs. (8) and (9). Hint: Multiply (8) from left with $\Phi_{el}^{\star}$ and integrate over the electronic coordinates $\underline{r}$.
2) Write down explicitly the determinantal wave function (Eq. (25)) for a system with three electrons occupying three spin orbitals ψ_a, ψ_b, and ψ_c. How many spin orbital products does this wave function contain?
3) Prove Eq. (28) by using the eigenvalue equation of the one-electron spin operator s_z:

$$s_z\alpha = \frac{1}{2}\alpha, s_z\beta = -\frac{1}{2}\beta \tag{65}$$

4) Show that the three two-electron wave functions

$$|\phi_a(1)\phi_b(2)| \tag{66}$$

$$\frac{1}{\sqrt{2}}[|\phi_a(1)\bar{\phi}_b(2)| + |\bar{\phi}_a(1)\phi_b(2)|] \tag{67}$$

$$|\bar{\phi}_a(1)\bar{\phi}_b(2)| \tag{68}$$

are products of an antisymmetric space and a symmetric spin function, while

$$\frac{1}{\sqrt{2}}[|\phi_a(1)\bar{\phi}_b(2)| - |\bar{\phi}_a(1)\phi_b(2)|] \tag{69}$$

is the product of a symmetric space and an antisymmetric spin function. Determine the M_S values for these wave functions. Can you guess the spin quantum numbers S for them?
5) Derive formulas for the energy expectation values of the two-electron wave functions given in problem 4.
6) Derive Eq. (37).
7) Derive Koopmans' theorem (Eq. (42)). Assume that the orbitals for the ion are the same as for the ground state of the neutral molecule, write down the one-determinant wave function for the ion, derive the energy expectation value for the ion and calculate the difference

$$IP(i) = E(ion) - E_{SCF} \tag{70}$$

8) Derive the matrix form (Eq. (45)) of the Hartree-Fock equation (41) by projecting to the basis function χ_μ. Hint (as in problem 1)): Insert ansatz Eq. (44) into Eq. (41), multiply from left by $\chi_\mu^{\star}$ and integrate over the coordinates of the electron.
9) Derive the secular equations (55). Hint: Write down the expectation value of the N-electron Hamiltonian H with the wave function (Eq. (54)) and vary the coefficients C_I.
10) Set up all possible Slater determinants Φ_I for a three-electron system (e.g. the Li atom), using a set of four (spatial) orbitals $\phi_i, i = 1, 2, 3, 4$. Determine their M_S values and their excitation levels with respect to the "ground state" determinant

$$|\phi_1\bar{\phi}_1\phi_2| \tag{71}$$

11) How many Slater determinants can be constructed for H_2O in a basis set of 24 basis functions? How many of them are doubly excited with respect to the Hartree-Fock determinant?

12) In the region of the equilibrium distance R_e, the ground state wave function for the H_2 molecule can be fairly well approximated by a single Hartree-Fock determinant

$$\Psi_1 = |\phi_1 \bar{\phi_1}| \tag{72}$$

where

$$\phi_1 = \frac{1}{\sqrt{2(1+S)}}(\chi_a + \chi_b) \tag{73}$$

is the lowest molecular orbital, expressed as a linear combination of the two 1s atomic orbitals at the two hydrogen atoms. (S is the overlap integral between χ_a and χ_b). Show that this wave function does not dissociate correctly into two H atoms. Hint: Consider the limit

$$\phi_1 \rightarrow \frac{1}{\sqrt{2}}(\chi_a + \chi_b) \quad \text{for } R \rightarrow \infty \tag{74}$$

Show further that the two-configuration wave function

$$\Psi_2 = \frac{1}{\sqrt{2}}(|\phi_1 \bar{\phi_1}| - |\phi_2 \bar{\phi_2}|) \tag{75}$$

$$\phi_2 = \frac{1}{\sqrt{2(1-S)}}(\chi_a - \chi_b) \tag{76}$$

dissociates correctly.

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